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Completion Report

**Spatial and Temporal Variability of
Phosphorus Retention and Release in
Riparian Forest Soils and Relationship to Soil**

by

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SPATIAL AND TEMPORAL VARIABILITY OF PHOSPHORUS RETENTION AND RELEASE IN RIPARIAN FOREST SOILS AND RELATIONSHIP TO SOIL PROPERTIES

ABSTRACT

Riparian zones have been found to remove P from surface runoff and can potentially act as filters of non-point source P pollution for surface waters. Soil properties important to P retention may vary along a soil drainage catena, as well as within a particular drainage class. Riparian areas are often characterized by drainage class gradients. Riparian forest soils were investigated in the spring and fall for their capacity to retain and/or release PO_4^{3-} -P using P-adsorption isotherms. Samples (300 on each date) were taken from a soil drainage catena in May and November of 1995 to examine the spatial and temporal variability of P retention/release. Three drainage classes were examined: moderately well (MWD), somewhat poorly (SPD), and poorly drained (PD) soil. The relationship between P retention/release capacity of the soil and soil properties measured at the same points, including soil organic matter, mass water content, pH, and oxalate-extractable Fe and Al content (Fe_{ox} , Al_{ox}) was examined.

The equilibrium P concentration at zero sorption (EPC_0) was determined from the isotherm for each sampling point (the lower the EPC_0 , the higher the P retention capacity). MWD soil had significantly different mean (CV) EPC_0 values of 1.0 (1.34) and 1.5 (1.03) mg P/L in May and November, respectively. SPD soil had the lowest retention capacity, with a mean EPC_0 value of 3.8 (0.49) in May and no P sorption apparent in November. PD soil had the highest P retention capacity for both sampling dates, with significantly different mean EPC_0 values of 0.5 (1.87) and 1.3 (1.13) mg P/L, respectively.

Phosphorus retention appeared to be controlled by organic matter and Fe_{ox} and Al_{ox} content. EPC_0 was positively correlated to soil organic matter for all three drainage classes on both sampling dates. Low EPC_0 values --high P retention capacity-- in MWD and PD soil corresponded with high Fe and Al values and increased with decreasing Fe_{ox} and Al_{ox} values. For SPD soil a high mean EPC_0 corresponded with low mean Fe_{ox} and Al_{ox} values. The relationship between EPC_0 and Fe_{ox} and Al_{ox} was described by a hyperbolic function for MWD and PD soil, but not for SPD soil.

The spatial structure of EPC_0 and soil properties were analyzed using semivariograms. Fe_{ox} , Al_{ox} , and organic matter exhibited spatial structure, as indicated by the strong fit of the data to the semivariogram model. By contrast, EPC_0 did not exhibit spatial structure at the sampling scale used for any of the drainage classes.

The results of our study indicate that within a riparian forest area, PD soil has the highest P retention capacity, followed by MWD soil, with SPD soil as a potential source of P depending on the time of year. It appears that the relationships between Fe_{ox} and Al_{ox} , organic matter content, and EPC_0 can be used to predict the P retention capacity of the soil in MWD and PD

soils

INTRODUCTION

Non-point source (NPS) nutrient pollution is a leading cause of water quality problems in the U.S. (Novotny 1989; USEPA 1973). Excessive nutrient loading from watersheds into surface waters can have negative ecological effects such as overstimulation of algal and aquatic plant growth in receiving waters (USEPA 1992). Agricultural practices in upland areas are a leading contributor of NPS nutrient contamination, particularly phosphorus (P), to freshwater ecosystems (USEPA 1992). Phosphorus is the limiting nutrient for primary productivity in most freshwater bodies (Schindler 1977). Increased loading of P into these ecosystems often leads to accelerated eutrophication (Wetzel 1983). More than 70% of the P load to freshwater systems is from land drainage via surface flow (Vought et al. 1994).

The interfaces between upland and freshwater ecosystems are known as riparian forest zones. These unique landscape features have distinct vegetation and soil characteristics. Their physical proximity results in extensive interaction with upland land uses and in filtering of nutrients moving from the upland areas to aquatic ecosystems (Lowrance 1991). Removal mechanisms for P in riparian areas include sorption of soluble P by surface soils as well as microbial and plant uptake (Lowrance et al. 1985; Richardson 1985).

Riparian zones have been investigated extensively on their ability to act as a buffer between these two ecosystems. Cooper and Gilliam (1987) found that about 50% of the P leaving agricultural fields appeared to be removed from runoff water in a riparian areas. According to Lowrance et al. (1984) 30% of total P entering a forested riparian area is retained. Cooper et al. (1986) and Nixon and Lee (1986), however, found both removal and release of soluble P from wetland soils. Omernick et al. (1981) suggested that forested buffer strips can become saturated with nutrients, thus becoming ineffective buffers over time. Although the results from these studies are contrasting, removal of dissolved P in surface runoff is considered to be generally effective (Lowrance et al. 1995).

A landscape-scale study was conducted within a riparian forest characterized by a soil drainage gradient to examine the spatial and temporal P retention/release capacity of the soils. Soil properties known to influence P retention/release, such as organic matter, soil moisture, pH, and Fe and Al content, likely exhibit spatial heterogeneity along this gradient. Seasonal changes in depth to water table, temperature, and microbial activity can influence soil properties such as levels of iron oxides and pH. Thus, soils within a riparian zone may remove/release P to varying degrees, depending on landscape position and time of year.

We measured the capacity of riparian forest soils to retain and/or releases PO_4^{3-} -P using P-adsorption isotherms in the spring and fall. Samples (300 on each date) were taken from a soil drainage catena in May and November of 1995 to examine the spatial and temporal variability of P retention/release. Three drainage classes were examined: moderately well (MWD), somewhat

poorly (SPD), and poorly drained (PD) soil. The relationship between P retention/release capacity of the soil and soil properties measured at the same points, including soil organic matter, mass water content, pH, and oxalate-extractable Fe and Al content (Fe_{ox} , Al_{ox}) was examined.

MATERIALS AND METHODS

Study site

The study area is located at the Peckham Farm Research Area of the University of Rhode Island (Kingston, RI) in the Chipuxet River watershed, within the larger Pawcatuck River Basin in southern Rhode Island. The area is forested and directly down gradient from a fallow field. The upland forest at the site is dominated by oak (*Quercus sp.*) grading to a red maple (*Acer rubrum*) swamp. The site is underlain by glacial outwash and contains a soil drainage catena. The soil in the upland portion of the site is mapped as a Hinkley sandy loam (sandy-skeletal, mixed, mesic Typic Udorthent) and grades to a Walpole sandy loam (sandy, mixed, mesic Aeric Haplaquept) and a Scarboro mucky sandy loam (sandy, mixed, mesic Histic Humaquept) (Soil Survey Staff 1981). Drainage classes of moderately well (MWD), somewhat poorly (SPD), and poorly drained (PD) were delineated using a modification of the criteria established by the Army Corps of Engineers (Wright and Sautter 1988).

Sampling

Soil samples were taken on 9 May and 8 November 1995 using a nested random stratified sampling scheme. A grid of 24 m in length by 15 m downslope was delineated to include the three drainage classes. The sampling scheme covered a 24 m x 5 m area in each drainage class, which was divided into five 5 m x 5 m subplots per drainage class. A total of 300 samples were taken at each sampling date, 100 samples per drainage class. Within each drainage class, 20 random samples from each subplot were taken, 10 of which were taken from two areas of 1 m by 1 m chosen randomly within each subplot. Nested samples were taken to capture spatial variations at a small scale. Sample points were surveyed to a common benchmark using a transit. The distance between samples for all drainage classes ranged from 7 cm to 24 m. The litter layer was removed and soil cores (5 cm dia) were taken from the top 5 cm, placed in plastic bags, and kept on ice in a cooler until transported to the laboratory, where they were stored in the dark at 4°C.

Soil Physical and Chemical Properties

Soil pH, organic matter content, and moisture content were determined within one week after the sampling date. Soil samples were homogenized manually by shaking before soil properties were determined.

Soil moisture content was determined gravimetrically after oven drying a 5.0-g sample of moist soil at 105°C for 6 h. Bulk density was determined by dividing the mass of the solids --

determined from the oven-dry weight of a fraction of the sample -- by the volume of the soil core (98 cm³). Soil pH was determined using a 1:2 soil/water ratio and a pH meter (Hendershot et al. 1993). Soil organic matter content was determined by loss on ignition at 550°C for 4 h (Karam 1993).

Oxalate-extractable Al and Fe (Al_{ox} and Fe_{ox}) were determined by atomic adsorption spectroscopy (Soil Conservation Service Staff 1972). Soil samples were air-dried for three days, sieved to pass a 2-mm-mesh sieve, and homogenized manually by shaking. For each sample, 1.0 g of air-dry soil was placed in a 250-ml plastic bottle and 100 ml of extractant was added. The extractant was a 0.2 M ammonium oxalate solution, adjusted to a pH of 3.0 with oxalic acid. The bottles were capped and shaken for 4 h at 175 rpm in the dark at room temperature (20 - 23° C). The resulting mixture was passed through a Whatman No. 42 filter, the filtrate placed in a plastic vial, and stored in the dark at room temperature for later analysis.

Phosphorus Retention/Release Capacity

Phosphorus adsorption isotherms were used to determine the ability of the soil to remove or release P according to the method of Guertal et al. (1991). Soil samples were air-dried for three days, sieved to pass a 2-mm-mesh sieve, and homogenized manually by shaking. For each sample, 1.0 g of air-dry soil was placed in a 20-ml plastic vial and 15 ml of a solution containing 0, 1, 3, 5, or 7 mg P L⁻¹ was added. Phosphorus solutions were prepared using NaH₂PO₄ in 0.5 M NaNO₃. The vials were capped and shaken for 24 h at 100 rpm in the dark at room temperature. The mixture was passed through a Whatman No. 42 filter and the filtrate analyzed for soluble reactive P colorimetrically using an automated nutrient analyzer (model RFA-300, Alpkem, Clackamas, OR).

Sorption isotherms were used to evaluate P removal/release capacity for each sampling point by plotting solution concentration after equilibration versus amount of P sorbed. From these data, the equilibrium P concentration at zero sorption (EPC_0) was determined for each sampling point at the point where the isotherm crosses the x-axis.

For each drainage class, five sample points were chosen randomly and analyzed in triplicate for evaluation of analytical uncertainty of EPC_0 determinations.

Statistical Analysis

Mean, median, standard deviation, and coefficient of variation (CV) were determined for all physical and chemical soil properties and EPC_0 values for each drainage class. Normality of the data was determined using the Kolmogorov-Smirnov test. For data sets that were not normally distributed, non-parametric statistical tests were used. An unpaired t-test or a Mann-Whitney rank sum test was used to assess differences in soil properties and EPC_0 values between seasons. A Kruskal-Wallis ANOVA on ranks was used to assess differences in soil properties and EPC_0 values among drainage classes. Multiple comparisons procedures were used to isolate

differences among EPC₀ values and soil properties --Dunn's method was used for EPC₀ values and the Student-Newman-Keuls method was used for other soil properties. Significant differences were evaluated at the 95% confidence level unless otherwise specified.

Scatter plots were created by plotting EPC₀ values against individual soil properties for each drainage class and linear and/or non-linear regression analysis was performed using SigmaPlot (version 5.0, Jandel Scientific, Corte Madera, CA). Stepwise multiple regression analysis of soil properties and EPC₀ values was performed to determine which combination of soil properties best explained variability in retention/release of P for each drainage class.

Geostatistical Analysis

Geostatistical analysis was used to model the spatial structure of EPC₀ and soil properties that affect P retention/release. Geostatistics assumes spatial dependence among sample points, which traditional statistical analyses tend to ignore (Rossi et al. 1992). This is important when investigating soil properties known to vary spatially and in identifying spatial distribution patterns that may exist in the field. The semivariogram is used to describe the spatial autocorrelation for a particular random variable measured on a sample spatial data set (Trangmar et al. 1985). It displays the change in the semivariance between two sample points as the distance between them increases. Semivariograms are calculated using the equation

$$\gamma (h) = \frac{1}{2} E [z(x_i) - z(x_i + h)]^2 \quad (1)$$

where $\gamma (h)$ is the semivariance, E is the expected squared distance between values of samples separated by lag distance h , and $z(x_i)$ and $z(x_i + h)$ are measured values at points x_i and $x_i + h$ (Trangmar et al. 1985).

Semivariograms were computed for each spatially-referenced soil property and EPC₀ values for each drainage class. GS+ (version 1.21, Gamma Design Software, Plainwell, MI), the geostatistical analysis program used, evaluates the semivariogram and suggests the model that best fits the data. In all cases, the spherical model, the most common variogram model used (Isaaks and Srivastava 1989), was used to fit the data. A lag spacing of 0.3 m, the average distance between sampling points (Isaaks and Srivastava 1989), was used in determining semivariograms for all soil properties for each of the three drainage classes.

RESULTS

Soil Physical and Chemical Properties

Soil physical and chemical properties were examined for temporal variation (Table 1). No significant differences were observed in mass water content, O.M., Al_{ox}, and Fe_{ox} in MWD soil between May and November. For SPD soil, O.M., Al_{ox}, and Fe_{ox} did not differ significantly between sampling dates, but mass water content was significantly lower and pH was significantly

higher in November. No significant differences in Al_{ox} and Fe_{ox} content between sampling dates were observed for PD soil. Otherwise, PD soil appeared to be more dynamic than the other drainage classes, with significantly lower mass water content, higher organic matter content, and higher pH in November than May.

Differences among drainage classes for each sampling date were also examined. Except for pH, all other soil properties differed significantly among drainage classes in both May and November (Table 1).

Distribution of P Retention/Release Capacity

P retention /release capacity of the soil was determined for all three drainage classes using P adsorption isotherms from which the equilibrium P concentration at zero sorption (EPC_0) was calculated. EPC_0 is the point at which the isotherm crosses the x-axis and represents the solution P concentration at which P adsorbs and desorbs at the same rate. A low EPC_0 represents a high P retention capacity; conversely, a high EPC_0 represents a low P retention capacity, indicating that added P would not be retained to the same extent as lower EPC_0 values, leaving more P in the labile and solution phases.

Significant differences in mean EPC_0 were observed between sampling dates for MWD and PD soils, with higher values observed in November (Table 2). We were not able to determine EPC_0 values for SPD soil in November because the initial P concentration of the soil exceeded the P concentration of the solutions added to the soil. Therefore, during the equilibration process, P was released from the soil into solution. Although the absence of P sorption by soil in November indicates that there was a difference in P sorption between sampling dates in SPD soil, we were not able to determine its magnitude or statistical significance.

Poorly drained soil had a significantly lower mean EPC_0 in May and November than MWD and SPD soils (Table 2). Somewhat poorly drained soil had the highest EPC_0 in May compared to MWD and PD soils. Overall, retention capacity of all three drainage classes was less in November than in May.

Triplicate analyses of samples were performed on five sampling points per drainage class to evaluate analytical uncertainty in the determination of EPC_0 values. The mean CV for MWD and PD soil ranged from 0.17 to 0.44, respectively (data not shown). These values are two to six times lower than the CVs observed for a drainage class (Table 2).

Relationship between EPC_0 and Soil Properties

EPC_0 was plotted against mass water content, O.M., pH, Fe_{ox} , and Al_{ox} to investigate relationships between P retention and soil physical and chemical properties. Soil organic matter was significantly and positively correlated to EPC_0 for all three drainage classes on both sampling dates (Table 3). Similarly, Fe_{ox} and Al_{ox} were significantly and negatively correlated to EPC_0 for

all drainage classes on both sampling dates, except for Al_{ox} in MWD soil in May.

Stepwise linear regression analysis was performed on data for each drainage class on both sampling dates to determine which combination of soil properties best predicted EPC_0 . In no case was the inclusion of more than one variable found to improve predictions of EPC_0 significantly.

Plots of EPC_0 versus Fe_{ox} and Al_{ox} suggested a non-linear relationship existed between these variables as shown for PD soil in November (Fig. 1). These data are representative of what was observed in MWD and PD soil on both sampling dates (data not shown). In general, EPC_0 appeared to be insensitive to changes in Fe_{ox} and Al_{ox} at low concentrations of these metals. There seemed to be a range of concentrations of these metals above which EPC_0 declined with increasing Fe_{ox} and Al_{ox} . This appeared to be the case for MWD and PD soil in May and November. SPD soil did not exhibit a similar relationship between EPC_0 and Fe_{ox} and Al_{ox} . The data were fit to the equation

$$EPC_0 = [1/(x^2 - a)]^{1/2} \quad (2)$$

where $x = Fe_{ox}$, Al_{ox} , or $Fe_{ox} + Al_{ox}$ ($mg\ g^{-1}$) and $a = a$ constant ($mg^2\ g^{-2}$). Parameter and RSS estimates are shown in Table 4. Similarly good fits were obtained whether Fe_{ox} , Al_{ox} , or the sum of Fe_{ox} and Al_{ox} were fit to equation 2, as indicated by similar RSS values.

The non-linearity of the relationship between EPC_0 values and Fe_{ox} and Al_{ox} suggested that perhaps another soil property was affecting P retention/release. We examined the possible involvement of O.M. using three dimensional plots to investigate the relationship between EPC_0 , organic matter content, and $Fe_{ox} + Al_{ox}$ (Fig. 2) for all drainage classes. Again, data are shown for PD soil in November for the sake of brevity, but the trend observed is representative of MWD and PD soil on both dates. Higher EPC_0 values generally occurred at high organic matter content and low levels of $Fe_{ox} + Al_{ox}$ and decreased with decreasing amounts of organic matter and increasing amounts of $Fe_{ox} + Al_{ox}$.

Spatial Analysis of EPC_0 and Soil Properties

Geostatistics was used to analyze the spatial structure of EPC_0 and soil physical and chemical properties for all drainage classes. Because we observed a relationship between EPC_0 and O.M., Fe_{ox} , and Al_{ox} , spatial analysis was performed to examine possible relationships among these properties. Model parameters, including range, sill, and nugget, Q , and r^2 are presented in Table 5. The nugget (C_0) represents unexplained variability attributable to analytical error or the chosen sampling scale. The sill (C), the value at which the semivariogram levels off, is the sample variance. This constant value occurs at a given separation distance known as the range. The ratio of the sill to the sum of the sill and nugget variance, Q , can be used to indicate the level of spatial structure that exists at the sampling scale used. Q is given by

$$Q = C/(C + C_0) \quad (3)$$

where C = sill and C_0 = nugget. The ratio ranges from 0 to 1; a value of 0 indicates that the variability is driven by the nugget variance -- a lack of spatial structure. As Q increases, more of the variance is explained by the semivariogram.

EPC_0 did not exhibit spatial structure at the sampling scale used for any of the drainage classes studied. The semivariograms had a weak fit (low r^2) and did not follow the general pattern of increasing semivariance with increasing distance (Fig. 3).

The spatial structure of Fe_{ox} was similar in all three drainage classes. The semivariograms had similar characteristics (Fig. 3) and the range was similar among drainage classes (2.97, 3.45, and 4.33 m for PD, MWD, and SPD soil, respectively) (Table 5). Values of Q for Fe_{ox} were 0.77, 0.69, and 0.98 for MWD, SPD, and PD soil, respectively. By contrast, the spatial structure of Al_{ox} differed among drainage classes (Fig. 3; Table 5). The value of Q was 0.36 for SPD soil, with a value of 0.99 for both MWD and PD soil. The highest range (8.78 m) was observed for SPD soil, followed by PD (3.55 m) and MWD soil (0.54 m) (Table 5). The spatial structure of soil organic matter also varied among drainage classes (Fig. 3). Range values decreased in the order MWD (8.65 m), SPD (2.99 m), and PD soil (0.51 m) (Table 5). Lower values of Q were observed for MWD (0.40) and SPD (0.49) soil than in PD (1.0) soil.

DISCUSSION

The high retention capacity --low EPC_0 values-- of MWD and PD soils indicate that larger amounts of phosphorus could be removed from solution by soil in these two drainage classes compared to SPD soil. The range of EPC_0 values observed in the present study (1.53-0.52 mg P/L) is within that observed for soils from other ecosystems. For example, Guertal et al. (1991) found EPC_0 values of 2 and 3 mg P/L for the top 2 cm of a field soil for a Hoytville silty clay loam and a Canfield silt loam, respectively. By contrast, in a riparian forest in North Carolina, Cooper and Gilliam (1987) observed mean (CV) EPC_0 values that ranged from 8.99 (0.34) in the forest edge to 31 (0.61) $\mu\text{g P/L}$ in the flood plain swamp. These values are much lower than the EPC_0 values observed in MWD, SPD, and PD soil in both May and November in our study (Table 2). Differences in EPC_0 values compared to those observed in our study, could be attributed to differences in vegetative cover. In the study of Cooper and Gilliam (1987), selective cutting of trees allowed the growth of a thick understory and floor vegetation. These management techniques have been suggested to maintain the successional stage and maintain nutrient filtering (Lowrance et al. 1983). The lower EPC_0 values of Cooper and Gilliam could also be attributed to differences in clay mineral content, since clay minerals are found in negligible quantities in Rhode Island soils (Wright and Sautter 1988).

The P retention capacity of soil is generally closely associated with the acid-extractable Fe and Al content of the soil (Karim et al. 1983; Richardson 1985; Abrams and Jarrell 1995). Extraction by ammonium oxalate is known to dissolve primarily the amorphous and poorly crystalline oxides of Fe and Al, which sorb large quantities of P from soil solution (Karim and Adams 1984; Sanyal et al. 1993; Abrams and Jarrell 1995). In the present study, the Fe_{ox} and Al_{ox}

content of the soil seems to exert a strong control on P removal. Low mean EPC_0 values --high retention capacity-- in PD and MWD soil corresponded with higher mean values of Fe_{ox} and Al_{ox} compared to SPD soil. PD soil, with the lowest mean EPC_0 for both sampling dates, had the highest mean of Fe_{ox} and Al_{ox} , while the lower P retention capacity in SPD soil was associated with lower mean Fe_{ox} and Al_{ox} values.

The relationship between Fe_{ox} and Al_{ox} and EPC_0 was not linear; rather, a hyperbolic function appeared to best describe the data. Such a relationship suggests that metals exert little control on P retention below a certain concentration of Fe_{ox} and/or Al_{ox} . For the three drainage classes, Fe_{ox} and Al_{ox} did not appear to affect EPC_0 below a range of 2 to 4 mg/g of these metals. When the levels of Fe_{ox} and Al_{ox} exceed this range, P retention appeared to be controlled directly by these properties. By contrast, the plot of EPC_0 versus Fe_{ox} or Al_{ox} for SPD soil showed much more scatter (data not shown) and no specific range of values for either Fe_{ox} or Al_{ox} (below which EPC_0 would not be affected) was apparent. The low levels of Fe_{ox} and Al_{ox} found in soil from this drainage class (Table 1) may be responsible for the absence of a hyperbolic relationship with EPC_0 .

P removal in soil is known to be affected by organic matter (Sanyal et al. 1993). Organic matter may coat Fe and Al oxides, thus blocking potential sorption sites and decreasing P adsorption (Stevenson 1994). Competition between humates and phosphate for adsorption sites may also decrease P adsorption (Stevenson 1994). Lopez-Hernandez (1986) found phosphate adsorption by tropical soils is reduced in the presence of organic anions. Guertal et al. (1991) investigated the depth dependence of P retention in soil and attributed the lower retention of P at the soil surface partly to higher organic matter content. Reddy et al. (1980) found increased EPC_0 values with increased application rates of organic residues in the form of animal wastes. Struthers and Sieling (1950) showed that under acidic conditions organic anions greatly reduced the amount of P adsorbed by Fe and Al.

For all drainage classes on both sampling dates, EPC_0 exhibited a significant, positive correlation with organic matter content, indicating that organic matter had a negative effect on P sorption capacity of the soil. The non-linearity of the relationship between EPC_0 and Fe_{ox} or Al_{ox} could result from the interactions of organic matter with Fe_{ox} and Al_{ox} . The non-linear relationship between Fe_{ox} or Al_{ox} and EPC_0 is seen at higher amounts of organic matter (Fig. 2). At lower levels of Fe_{ox} and Al_{ox} , the effects of organic matter on P retention --high EPC_0 values-- are apparent, whereas at higher levels of Fe_{ox} and Al_{ox} , organic matter appears to have no effect. At low levels of Fe_{ox} and Al_{ox} , organic acids could out-compete phosphate for adsorption sites, but at higher levels of Fe_{ox} and Al_{ox} , more adsorption sites are available, thus reducing competition between organic matter and phosphate.

Spatial and Temporal Variability

Classical statistics assumes that one sample point is independent of all other sample points. In landscape-scale studies it seems more appropriate to assume spatial dependence of processes,

especially in soil, for which properties are known to vary systematically as a function of topography, vegetation, and parent material (Upchurch and Edmonds 1991). Geostatistics, which assumes spatial dependence of sample points, was chosen to examine the spatial structure (spatial relationship) of P retention/release and soil properties that affect P retention and release.

There was a lack of spatial structure of EPC_0 among the drainage classes as described by the semivariogram (Fig. 3). Although the model parameters (Table 3) suggest that the variability is explained by the model -- indicated by the lack of nugget variance -- EPC_0 showed extreme sensitivity to changes in parameters. The chosen lag spacing of 0.305 m, equal to the average distance between points, could not be used for MWD and SPD soil. The range values for these drainage classes were 0.25 and 0.32 m for MWD and SPD soil, respectively. These distances are very close to the shortest distance between sampling points (0.40 m), which implies lack of spatial structure. It may also indicate that the sampling scale and/or the size of the sample itself was not sufficiently small. This suggests that perhaps another property affecting P retention/release may vary at a smaller scale.

Although retention capacity remained low for both MWD and PD soil, there were differences between sampling dates. In November, P retention was lower for all drainage classes as indicated by higher EPC_0 values. As mentioned previously, no P sorption occurred in SPD soil in November. This decrease in P retention could perhaps be driven by the change in organic acids due to leaching of organic matter acids prior to sampling. These organic ions could be outcompeting phosphate anions for sorption sites (Lopez-Hernandez et al. 1986, Stevenson 1994). Other studies in riparian forests found no difference in P retention between seasons. Lowrance et al. (1984) found total P and dissolved phosphate (DP) showed almost no change between seasons for a riparian forest in an agricultural watershed in Georgia. Osborne and Kovacic (1993) found no effect of season on the mean concentration of DP in a riparian forest in Illinois. However, Peterjohn and Correll (1984) observed that peak output of *ortho*-phosphate for a watershed in Maryland occurred in the spring.

CONCLUSIONS

Poorly drained soil, with the lowest mean EPC_0 in May and November, had the highest P retention capacity in the soil drainage catena. Moderately well drained soil also had potential to act as a sink for P. However, once the concentration of the surface water exceeds the EPC_0 , the soil may contribute P to the overlying water. EPC_0 for SPD soil in May, although much higher than MWD and PD, indicated this drainage class as a sink for P. However, this area may have become saturated with P and no longer acts as a sink but rather a source of P. The P retention capacity of MWD and PD decreased in November.

The P retention capacity of the soil (EPC_0) appeared to be controlled by organic matter content and Fe- and Al-oxides. A significant positive relationship was observed between EPC_0 and organic matter, whereas the relationship between EPC_0 and Fe_{ox} and Al_{ox} was non-linear. There appeared to be a range of concentrations of the metals, above which EPC_0 exhibited consistently low values. Higher values of EPC_0 occurred with high amounts of organic matter

and low levels of Fe_{ox} and Al_{ox} .

Geostatistical analysis showed that EPC_0 exhibited a lack of spatial structure at the sampling scale used. However, because the sampling intensity of the present study was high, it appears that classical statistical tests can be used to determine P retention capacity at this site.

Identifying areas within riparian forest zones with the greatest removal will allow for more efficient use of these landscape features for water quality improvement. The established relationships of organic matter content, Fe_{ox} , and Al_{ox} content, with EPC_0 will target areas for maximum P removal.

LITERATURE CITED

- Abrams, M.M., and W.M. Jarrell. 1995. Soil phosphorus as a potential nonpoint source for elevated stream phosphorus levels. *J. Environ. Qual.* 24:132-138.
- Alpkem Corp. 1986. RFA-300 Operator's manual. Alpkem Corp. Clackamas, OR.
- Cooper, J.R., J.W. Gilliam, and T.C. Jacobs. 1986. Riparian areas as controls of nonpoint pollutants. p.166-190. *In* D.C. Correll (ed.) *Watershed research perspectives*. Smithsonian Institute Press, Washington, D.C.
- Cooper, J.R., and J.W. Gilliam. 1987. Phosphorus redistribution from cultivated fields into riparian areas. *Soil Sci. Am. J.* 51:1600-1604.
- Guertal, E.A., D.J. Eckert, S.J. Traina, and T.J. Logan. 1991. Differential phosphorus retention in soil profiles under no-till crop production. *Soil Sci. Soc. Am. J.* 55:410-413.
- Hendershot, W.H., H. Lalonde, and M. Duquette. 1993. Soil reaction and exchangeable acidity. p. 141-145. *In* M.R. Carter (ed.) *Soil sampling and methods of analysis*. Canadian Society of Soil Science. Ontario, Canada.
- Isaaks, E.H., and R.M. Srivastava. 1989. *An introduction to applied geostatistics*. Oxford University Press, Oxford, England.
- Karam, A. 1993. Chemical properties of organic soils. p. 459-471. *In* M.R. Carter (ed.) *Soil sampling and methods of analysis*. Canadian Society of Soil Science, Ontario, Canada.
- Karim, M.I., and W.A. Adams. 1983. Relationships between sesquioxides, kaolinite, and phosphate sorption in a catena of oxisols in Malawi. *Soil Sci. Soc. Am. J.* 48:406-409.
- Lowrance, R.R., R.L. Todd, and L.E. Asmussen. 1983. Waterborne nutrient budgets for the riparian zone of an agricultural watershed. *Agric. Ecosystems Environ.* 10:371-384.
- Lowrance, R.R., R.L. Todd, and J. Fail Jr. 1984. Riparian forests as nutrient filters in agricultural watersheds. *BioSci.* 34:374-377.
- Lowrance, R.R., R. Leonard, and J. Sheridan. 1985. Managing riparian ecosystems to control nonpoint pollution. *J. Soil Water Conserv.* 40:87-91.
- Lowrance, R.R. 1991. Effect of buffer systems on the movement of N and P from agriculture to streams. p. 87-96. *In* NPo-forskning fra Miljøstryrelsen. Conf. contributions. International conference on N, P, and organic matter. Miljøstryrelsen, Helsingør, Denmark.
- Lowrance, R., L.S. Altier, J.D. Newbold, R.R. Schnabel, P.M. Groffman, J.M. Denver, D.L. Correll, J.W. Gilliam, J.L. Robinson, R.B. Brinfield, K.W. Staver, W. Lucas, A.H. Todd. 1995. Water quality functions of riparian forest buffer systems in the Chesapeake Bay Watershed. Ches. Bay Program Rep. 134/95, EPA 903-R-95-004.
- Nixon, S.W. and V. Lee. 1986. Wetlands and water quality: A regional review in recent research in the United States on the role of freshwater/saltwater wetlands as sources, sinks, and retransformers of nitrogen, phosphorus, and various heavy metals. Tech. Rep. Y-86-2, U.S. Army Eng. Waterways Exp. Stn., Vicksburg, MS.
- Novotny, V., and G. Chesters. 1989. Delivery of sediment and pollutants from nonpoint sources: A water quality perspective. *J. Soil Water Conserv.* 44:568-576.
- Omernick, J.M., Abernathy, A.R., and L.M. Male. 1981. Stream nutrient levels and proximity of agricultural and forest land to streams: Some relationships. *J. Soil Water Conserv.* 36:227-231.

- Osborne, L.L., and D.A. Kovacic. 1993. Riparian vegetated buffer strips in water-quality restoration and stream management. *Freshwater Biol.* 29:243-258.
- Peterjohn, W.T., and D.L. Correll. 1984. Nutrient dynamics in an agricultural watershed: Observations on the role of a riparian forest. *Ecol.* 65:1466-1475.
- Reddy, K.R., M.R. Overcash, R. Khaleel, and P.W. Westerman. 1980. Phosphorus adsorption-desorption characteristics of two soils utilized for disposal of animal wastes. *J. Environ. Qual.* 9:86-92.
- Richardson, C.J. 1985. Mechanisms controlling phosphorus retention capacity in freshwater wetlands. *Sci.* 228:1424-1427.
- Rossi, R.E., D.J. Mulla, A.G. Journel, and E.H. Franz. 1992. Geostatistical tools for modeling and interpreting ecological spatial dependence. *Ecol. Monogr.* 62:277-314.
- Sanyal, S.K., S.K. De Datta, P.Y. Chan. 1993. Phosphate sorption-desorption behavior of some acidic soils in South and Southeast Asia. *Soil Sci. Soc. Am. J.* 57:937-945.
- Schindler, D.W. 1977. Evolution of phosphorus limitation in lakes. *Sci.* 195:260-262.
- Soil Conservation Service Staff. 1972. Soil survey laboratory methods and procedures for collecting soil samples. USDA-SCS Soil Survey Investigations Report No. 1. U.S. Gov. Print. Office, Washington, D.C.
- Soil Survey Staff. 1981. Soil survey of Rhode Island. USDA-Soil Conservation Service, U.S. Gov. Print. Office, Washington, D.C.
- Stevenson, F.J. 1994. Humus chemistry: Genesis, composition, reactions. 2nd ed. John Wiley & Sons, Inc., New York, N.Y.
- Struthers, P.H., and D.H. Sieling. 1950. Effect of organic anions on phosphate precipitation by iron and aluminum as influenced by pH. *Soil Sci.* 69:205-213.
- Trangmar, B.B., R.S. Yost, and G. Uehara. 1985. Application of geostatistics to spatial studies of soil properties. *Adv. Agron.* 38:45-94.
- Upchurch, D.R., and W.J. Edmonds. 1991. Statistical procedures for specific objectives. p.49-71. *In* M.J. Mausbach and L.P. Wilding (eds.) *Spatial variabilities of soils and landforms.* SSSA Spec Publ. 28. SSSA, Madison, WI.
- U.S. Environmental Protection Agency. 1973. Methods for identifying and evaluating the nature and extent of nonpoint sources of pollutants. Office of Air and Water Programs, U.S. Environ. Protection Agency, Washington, D.C.
- U.S. Environmental Protection Agency. 1992. Report to Congress: National water quality inventory. Washington D.C.
- Vought, B.M., J. Dahl, C.L. Pederson, and J.O. Lacoursiere. 1994. Nutrient retention in riparian ectones. *Ambio* 23:342-348.
- Wetzel, R.G. 1983. *Limnology.* 2nd ed. Saunders College Publ., Philadelphia, PA.
- Wright, W.R., and E.H. Sautter. 1988. Soils of Rhode Island landscapes. Univ. Rhode Island Agric. Expt. Sta. Bull. No.429.

FIGURE LEGENDS:

Fig. 1. Relationship between EPC_0 and Fe_{ox} (A), Al_{ox} (B), and $Fe_{ox} + Al_{ox}$ (C) for PD soil in November.

Fig. 2. 3-D mesh plot of EPC_0 versus O.M. content and $Fe_{ox} + Al_{ox}$ for PD soil in November.

Fig. 3. Semivariograms of EPC_0 (A), Fe_{ox} (B), Al_{ox} (C), O.M. content (D) for MWD, SPD, and PD soil in May.

PD - November 1995

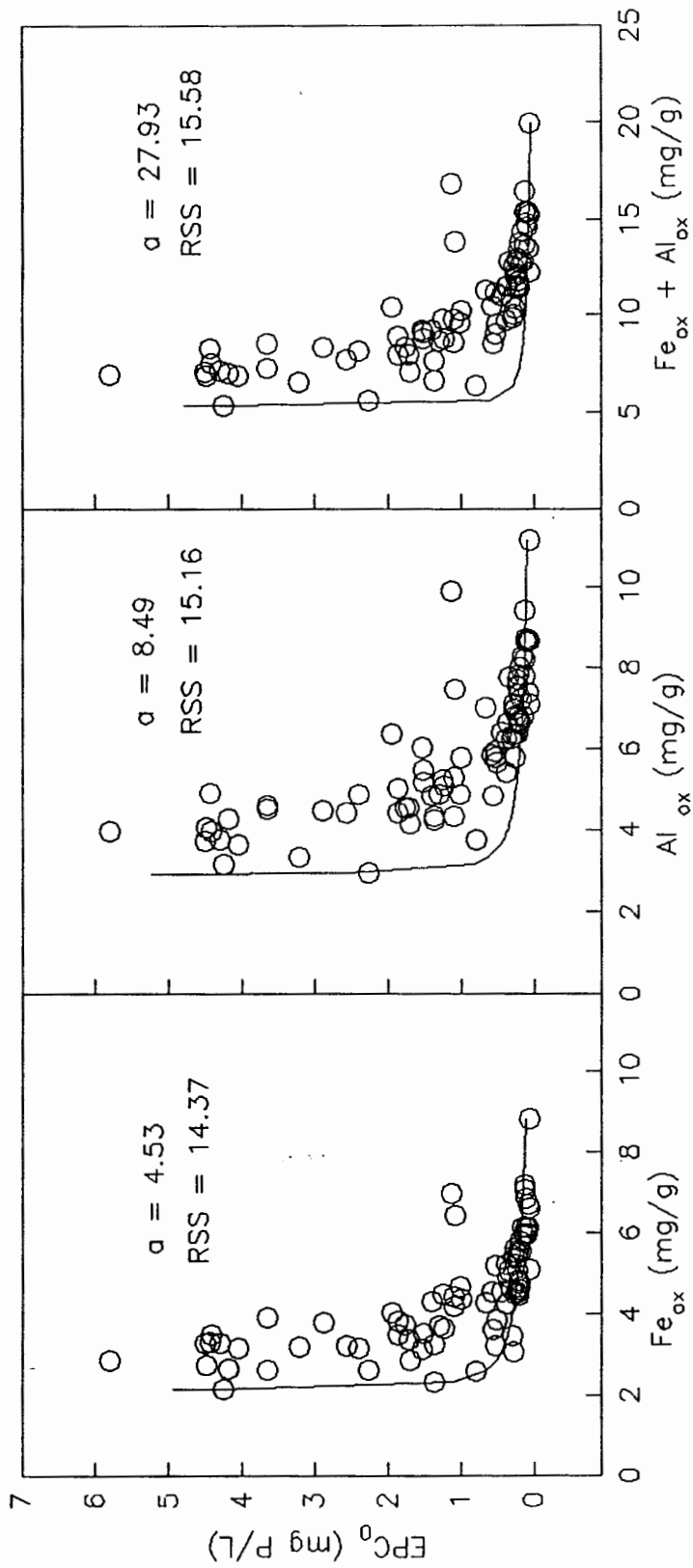
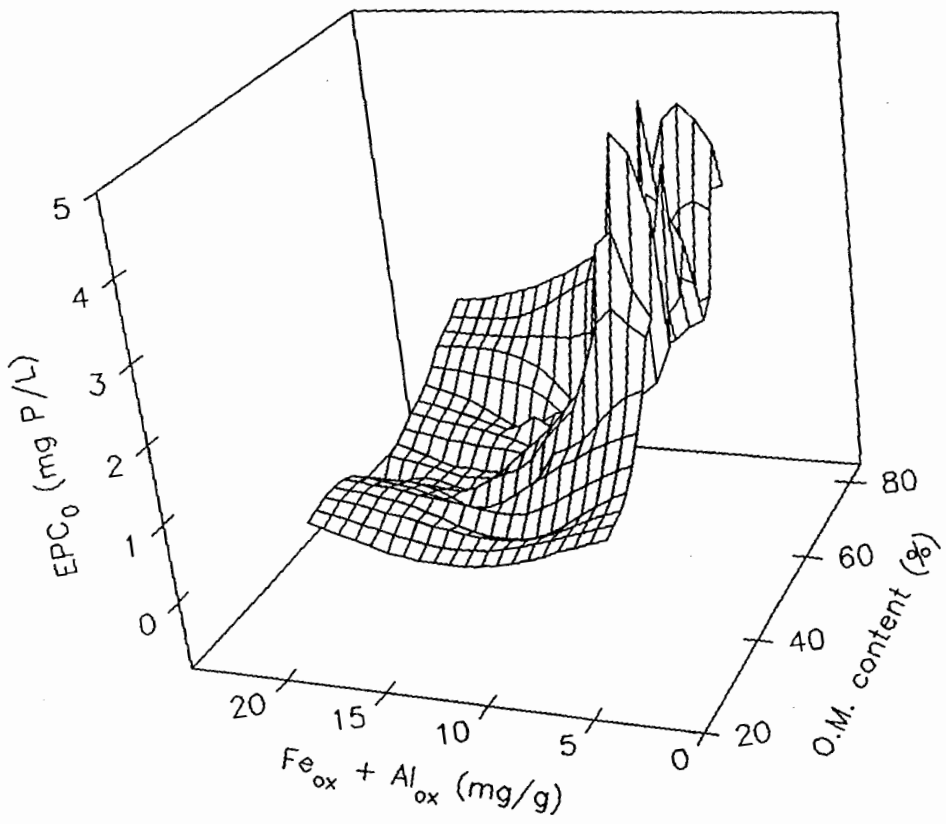
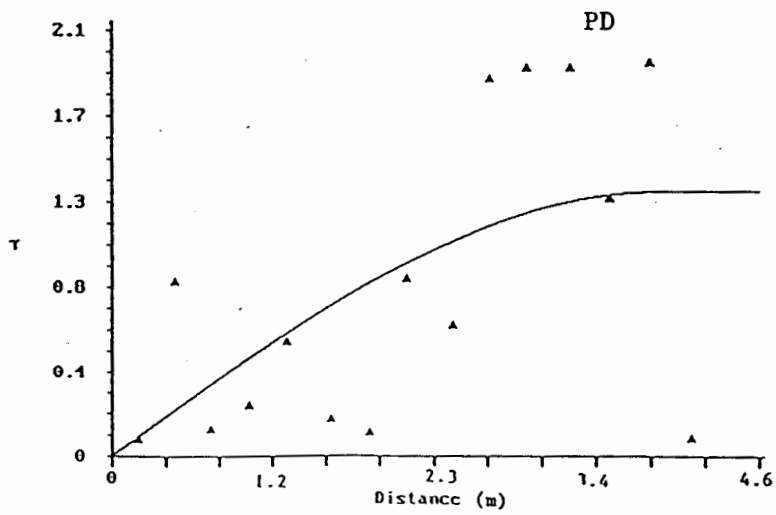
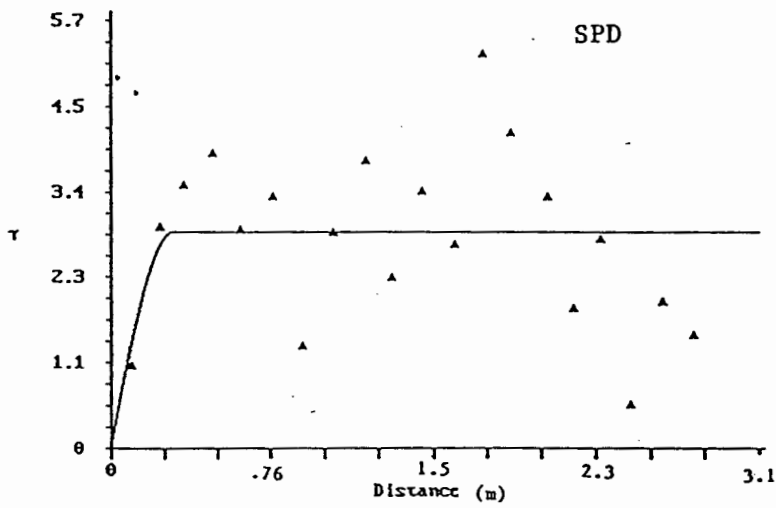
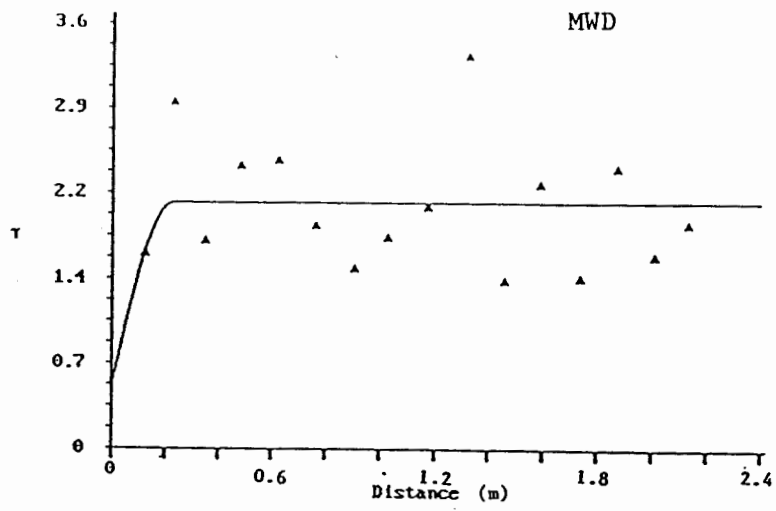
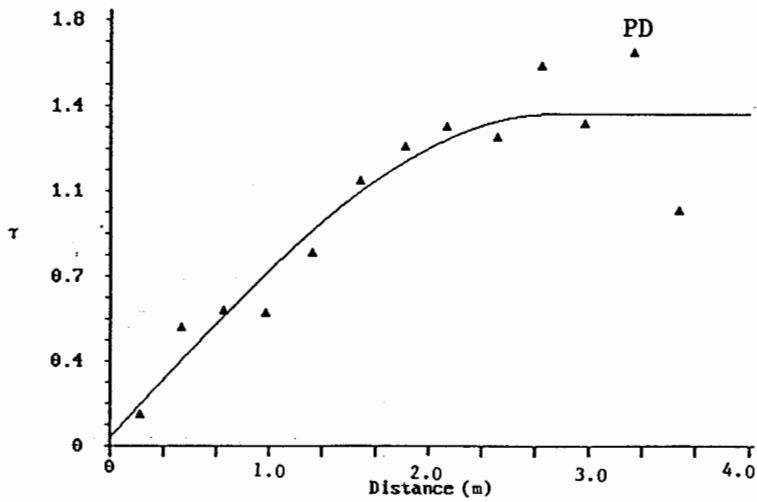
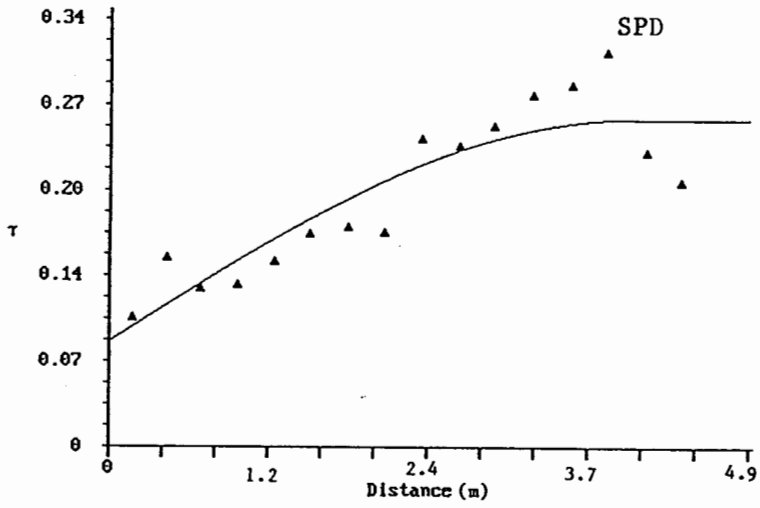
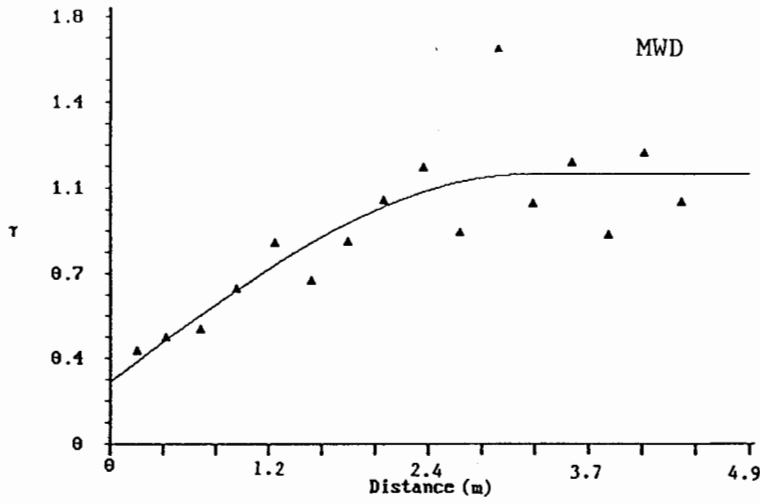


Fig. 2







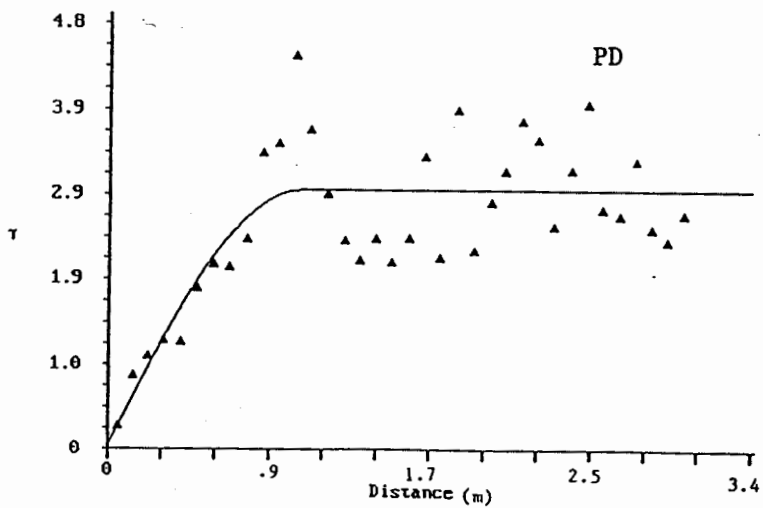
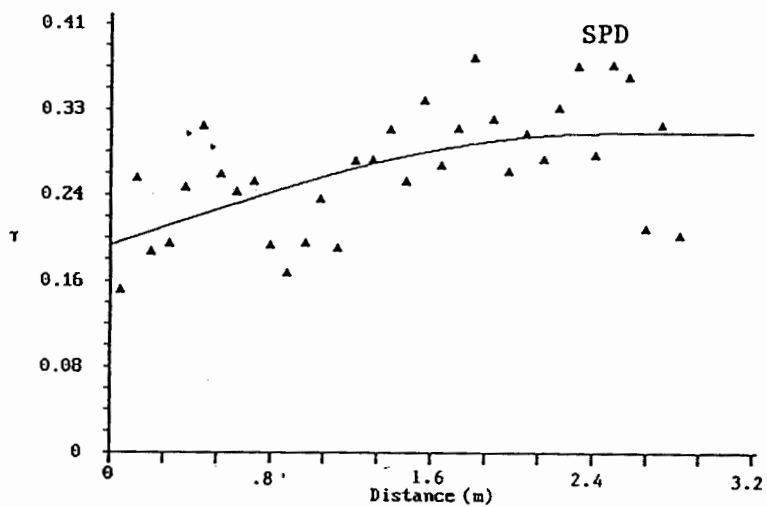
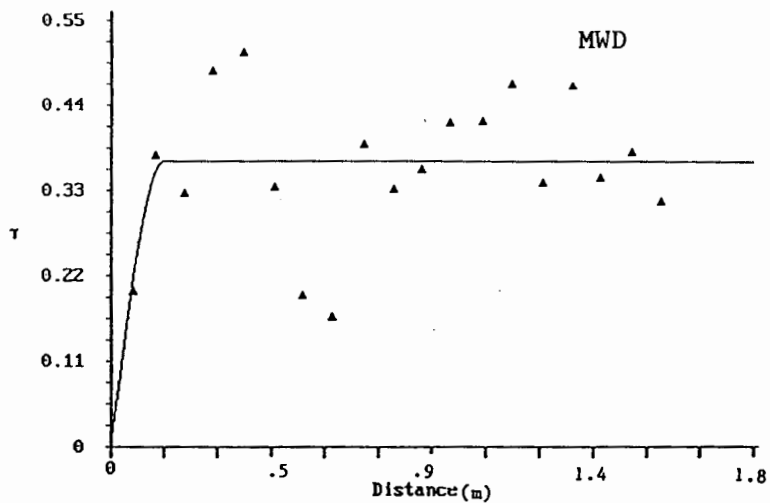


Fig. 3D

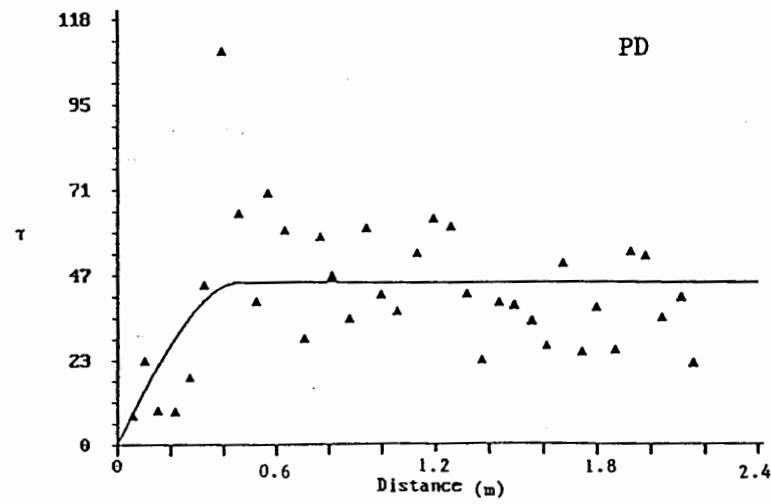
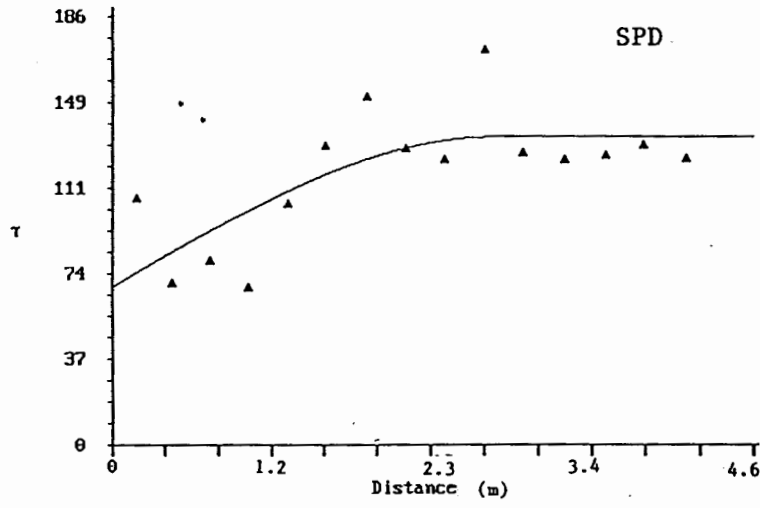
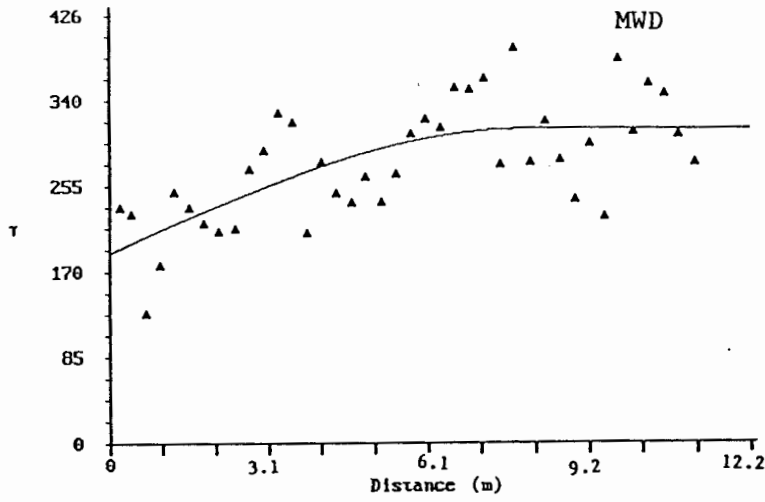


TABLE 1

Mean, standard deviation (STD), and coefficient of variation (CV) of soil properties for MWD, SPD, and PD soil in May and November.

Soil drainage class	Date		Mass water content (%)	O. M. content (%)	pH	Al _{ox} (mg/g)	Fe _{ox} (mg/g)
MWD	May	Mean ¹	87.5† ² ,a ³	33.8†,a	3.8†,a	2.19†,a	2.16†,a
		Median	76.4	72.7	3.8	2.14	1.84
		STD	42.7	16.8	0.2	0.61	0.92
		CV	0.5	0.50	0.1	0.28	0.43
	Nov.	Mean	79.1†,x	35.5†,x	4.1†,x	2.18†,x	2.58†,x
		Median	72.7	32.8	4.2	2.13	2.46
		STD	35.7	15.7	0.2	0.52	0.92
		CV	0.5	0.4	0.1	0.24	0.3
SPD	May	Mean	191.0	63.1 b	3.8	1.97	1.63
		Median	195.1	66.0	3.8	1.96	1.62
		STD	43.4	11.7	0.2	0.2	0.54
		CV	0.23	0.19	0.1	0.1	0.33
	Nov.	Mean	155.8†,y	61.9†,y	4.0†,y	2.04†,y	1.92†,y

		Median	157.9	63.9	4.0	2.06	1.92
		STD	36.1	9.9	0.3	0.50	0.46
		CV	0.2	0.2	0.1	0.25	0.24
PD	May	Mean	241.8†,c	59.8†,c	3.7†,c	5.16†,c	3.51†,c
		Median	245.4	59.7	3.6	5.07	3.38
		STD	35.7	7.1	0.2	1.84	1.17
		CV	0.15	0.12	0.1	0.36	0.33
	Nov.	Mean	219.9‡,z	62.3‡,z	4.2‡,z	5.60‡,z	4.14‡,z
		Median	212.5	62.5	4.2	5.46	3.9
		STD	48.4	8.7	0.2	1.96	1.51
		CV	0.2	0.1	0.05	0.35	0.37

¹ n = 100 for all soil properties for all drainage classes on both sampling dates.

² Values within a drainage class followed by the same symbol within a column are not significantly different, using a t-test for mass water content (SPD), bulk density (SPD), Al_{ox} (SPD, PD), and Fe_{ox} (SPD, PD), otherwise a Mann-Whitney rank sum test.

³ Values among drainage classes for each date followed by the same letter within a column are not significantly different, using a Kruskal-Wallis ANOVA on ranks test.

TABLE 2

1
2 Mean, median, standard deviation (STD), and coefficient of variation (CV) of EPC₀ for MWD, SPD, and PD in May and
3 November, 1995.

4	MWD			SPD			PD		
	5 Date	May	November	May	November	November	May	November	
6		EPC ₀ (mg P L ⁻¹)							
7	Mean	1.01†,a ^{1,2}	1.53‡,x	3.80b	ND ³	ND ³	0.52‡,c	1.26‡,y	
8	Median	0.36	1.09	3.93	ND	ND	0.17	0.55	
9	STD	1.35	1.57	1.85	ND	ND	0.98	1.42	
10	CV	1.34	1.03	0.49	ND	ND	1.87	1.13	
11	n	80	66	61	ND	ND	74	82	

12 ¹ Values within a drainage class followed by the same symbol are not significantly different.

1 ² Values among drainage classes for each date followed by the same letter are not significantly different.

2 ³ Not determined.

TABLE 3

1
2 Coefficient of determination (r^2) of EPC₀ versus individual soil physical and chemical properties.

3 Soil drainage	Date	Mass water	O.M.	pH	Al _{ox}	Fe _{ox}
4 class		content (%)	content (%)		(mg/g)	(mg/g)
5 MWD	May	0.170*** ¹	0.151***	0.009	0.037	0.105*
	Nov	0.154*	0.226***	0.175***	0.249***	0.299***
6 SPD	May	0.303***	0.199***	0.064	0.348***	0.234***
	Nov	ND ²	ND	ND	ND	ND
7 PD	May	0	0.109*	0	0.317***	0.287***
	Nov	0	0.073*	0.064	0.508***	0.417***

8 ¹ *, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

9 ² Not determined

TABLE 4

Parameter estimates for a non-linear model (eq. 2) describing the relationship between EPC_0 and Fe_{ox} , Al_{ox} , and $Fe_{ox} + Al_{ox}$.

Soil drainage class	Date	Variable included	a ($mg^2 g^{-2}$)	RSS ¹
MWD	May	Fe_{ox}	1.14	11.71
		Al_{ox}	1.82	11.45
		$Fe_{ox} + Al_{ox}$	8.77	11.81
	Nov	Fe_{ox}	1.55	14.38
		Al_{ox}	1.71	13.81
		$Fe_{ox} + Al_{ox}$	7.58	15.54
PD	May	Fe_{ox}	2.68	6.73
		Al_{ox}	4.54	6.78
		$Fe_{ox} + Al_{ox}$	21.41	8.13
	Nov	Fe_{ox}	4.53	14.37
		Al_{ox}	8.49	15.16
		$Fe_{ox} + Al_{ox}$	27.93	15.58

¹ Residual sum of squares.

TABLE 5

Geostatistical model parameters of O.M., Fe_{ox} and Al_{ox} content.

	Drainage class	Soil property	Range (m)	Sill	Nugget	Q	r ²
1							
2							
3							
4							
5	MWD	O.M.	8.7	312.5	188.4	0.40	0.45
		Fe _{ox}	3.45	1.14	0.26	0.77	0.70
		Al _{ox}	0.54	0.367	0.001	0.99	0.16
6	SPD	O.M.	2.99	134.4	68.6	0.49	0.53
		Fe _{ox}	4.33	0.26	0.08	0.69	0.80
		Al _{ox}	8.78	0.31	0.20	0.36	0.34
7	PD	O.M.	0.51	45.7	0.1	1.0	0.26
		Fe _{ox}	2.97	1.41	0.03	0.98	0.87
		Al _{ox}	3.55	2.95	0.03	0.99	0.63